

4

MICROWAVE SPECTROSCOPY

Introduction

Spectroscopy in the microwave region is called microwave spectroscopy and is concerned with the study of rotating molecules. In other words microwave spectroscopy deals with rotational spectra. This spectra is due to transitions between different rotational levels. If the transition occurs within the same vibrational level we obtain a pure rotational spectra. Actually the region of spectra would be in the microwave or far infrared region. The study of rotational spectra provides a direct method for the evaluation of molecular parameters. This study of rotational spectra has been made use of in the construction of the microwave oven.

Classification of molecules

We know that the rotation of a body can be described in terms of rotational inertia called moment of inertia (I). The same can also be used in the case of molecules. To describe a molecule we require three principal moments of inertia I_A , I_B and I_C about three mutually perpendicular axes. In general the three axes are chosen in such a way that $I_A < I_B < I_C$. Based on the relative values of principal moments of inertia I_A , I_B and I_C , the molecules are classified into four groups. They are (1) linear molecules (2) symmetric tops (3) spherical tops and (4) asymmetric tops.

1. Linear molecules

The molecules in which atoms are arranged in a straight line are called linear molecules. HCl , CO_2 , OCS , HCN , C_2H_2 etc. are linear molecules.

Here I_A is the moment of inertia of the molecule about the molecular axis, I_B is the moment of inertia about an axis passing through the centre of gravity of the molecule and perpendicular to the molecular axis and I_C is the moment of inertia about an axis passing through the centre of gravity perpendicular to both A and B axes. See figure 4.1.

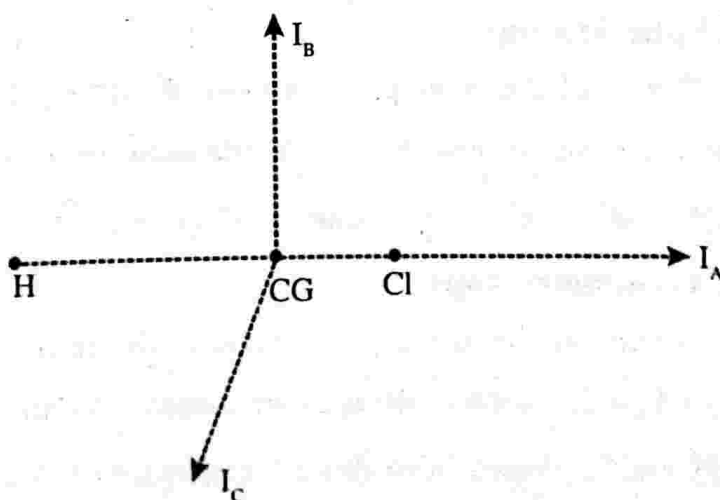


Figure 4.1

It is from the definition of I_A , I_B and I_C it is obvious that $I_A = 0$ and $I_B = I_C$. Thus a linear molecule is described by $I_A = 0$ and $I_B = I_C$.

2. Symmetric tops

In symmetric tops molecules $I_A \neq 0$ and $I_B = I_C$. Consider a molecule such as CH_3Cl , where the three hydrogen atoms are attached (bonded) tetrahedrally to the carbon as shown below.

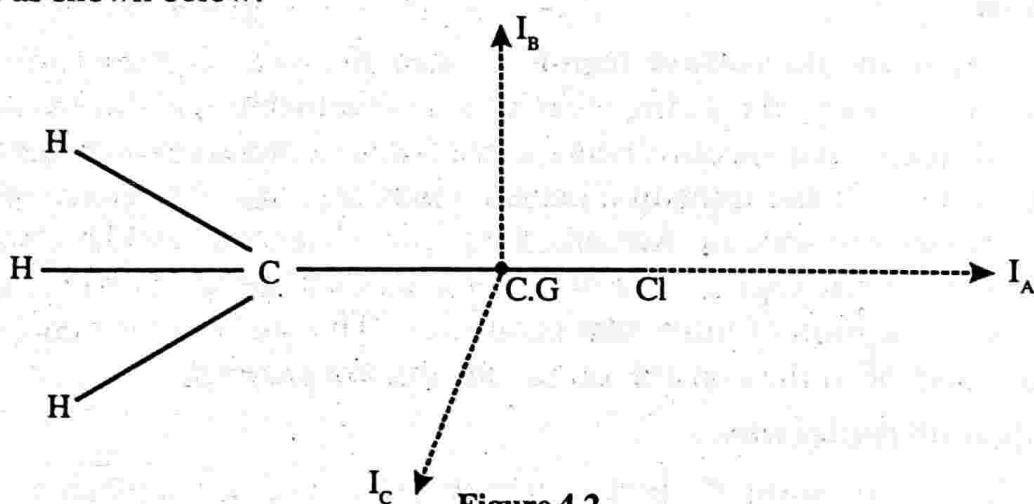


Figure 4.2

A molecule of this type spinning about A axis resembles a spinning top and hence the name symmetric top. This type molecules can further be divided into two classes depending on whether I_A is smaller or greater with respect to I_B .

If $I_A < I_B = I_C$ they are called prolate symmetric top and if $I_A > I_B = I_C$ they are called oblate symmetric top. CH_3Cl , CH_3F , CH_3CN , NH_3 etc. are examples of prolate symmetric top molecules and BF_3 , BCl_3 are examples of oblate symmetric top molecules.

3. Spherical tops

When all the principal moments of inertia of a molecule are equal, it is called a spherical top molecule. i.e., A spherical top molecule is described by $I_A = I_B = I_C$. CH_4 , SF_6 , CCl_4 are examples of spherical tops.

4. Asymmetric tops

When all the principal moments of inertia of a molecule are different i.e., $I_A \neq I_B \neq I_C$, such molecules are called asymmetric top molecule. H_2O , CH_3OH , CH_2OHCl (vinyl chloride) are examples of this. Majority of the molecules belong to this group.

Rotational spectra

The rotational energy like all other forms of molecular energy is also quantised. This means that a molecule cannot have any arbitrary amount of rotational energy but its energy is limited to a certain definite values depending on the shape and size of the molecule. These permitted values of energy are called rotational energy levels. In principle rotational energy levels can be calculated by solving the Schrödinger equation for the system represented by that molecule. For simple molecules solving Schrödinger equation is straight forward but tedious, while for complicated system of molecules it is impossible to solve Schrödinger equation without approximations. In our study we are not bothered about solving Schrödinger equation but we take the results of existing solution and point out where reasonable approximation may lead.

Interaction of radiation with rotating molecule

When an electromagnetic radiation of proper frequency interacts with rotating molecule, rotational energy transition takes place. In this way we get a rotation spectrum. For this to happen the molecule must have a permanent dipole moment.

Consider a diatomic molecule having a dipole moment which will be along the bond. When the molecule rotates about an axis perpendicular to the bond, the direction of the dipole moment changes continuously resulting in a periodic variation in a given direction. This generates a fluctuating electric field which interacts with the electric field of the electromagnetic radiation leading to pure rotational spectrum. This shows that energy can be exchanged only if the molecule has a permanent

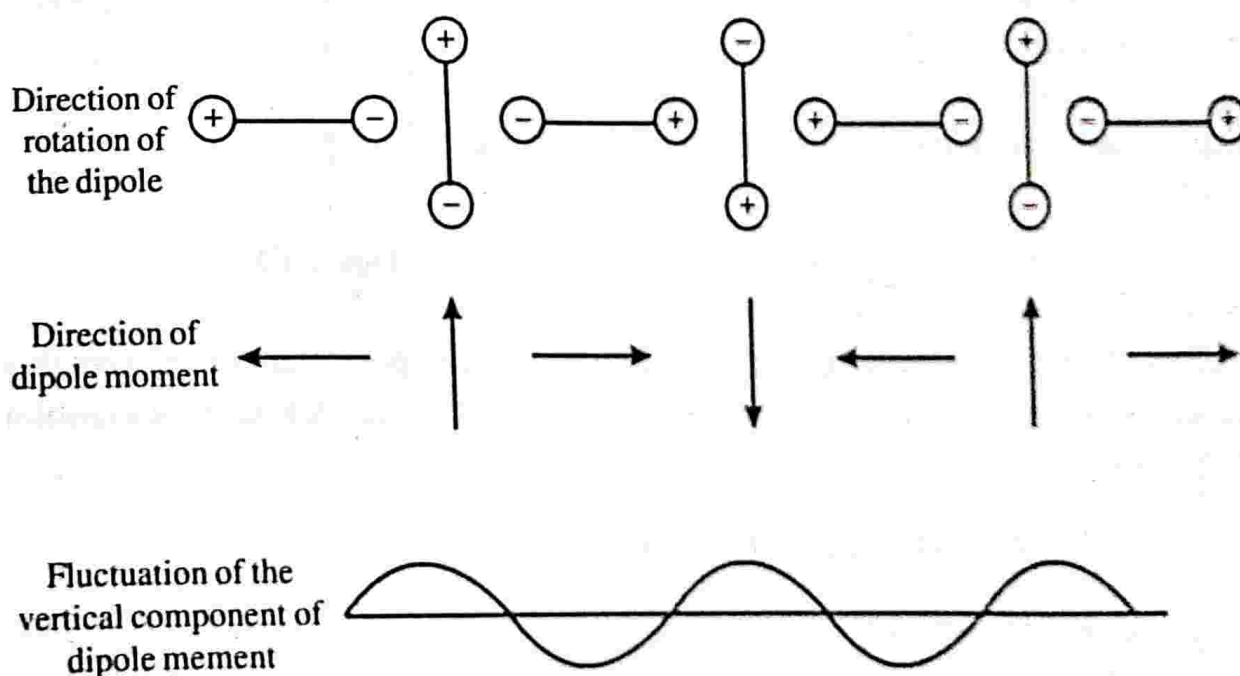


Figure 4.3

dipole moment. If the permanent dipole moment is zero there will not be any periodic variation. In the case of symmetric top and spherical top molecules, no rotational spectra are observed since they have no dipole moment owing to their symmetry.

If ψ_i and ψ_j are the wave functions for the rotational states i and j , the transition moment μ_{ij} is given by

$$\mu_{ij} = \int \psi_i^* \mu \psi_j d\tau$$

$\mu_{ij} \neq 0$ only if the molecule has a permanent dipole moment. The allowed transitions are governed by the selection rule $\Delta J = \pm 1$, J is the rotational quantum number.

Rigid diatomic molecules (Rigid rotator)

Rigid rotator is the simplest model of a molecule. It consists of two atoms of masses m_1 and m_2 connected by a rigid bond of length r . This is a two body problem and can be reduced to an equivalent one body problem, consisting of reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{ at a distance } r \text{ from the centre}$$

of mass of the two atoms. The only motion that can be quantised is the molecule about the axis passing through the centre of mass and perpendicular to the line joining the two atoms. Such a model is called a rigid rotator in a plane.

Motion of such a motion can be described in terms of a single coordinate θ , the angle of rotation of the axis of the molecule. In a such a case, the potential energy remains constant during the motion, since the distance does not change. Angular momentum of the rotator is

$$L = \mu v r = \mu r \cdot v = \mu r \cdot r\omega = \mu r^2 \omega$$

$$L = I\omega \quad (\mu r^2 = I)$$

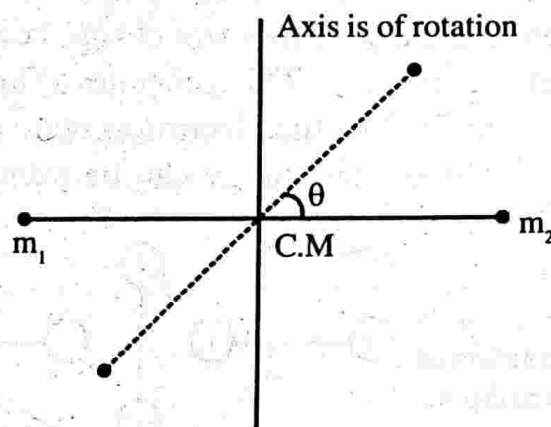


Figure 4.4

where I is the moment of inertia of the rotator about the axis of rotation. According to Bohr - sommerfeld quantisation rule, we have

$$\oint L d\phi = nh$$

$$\int_0^{2\pi} L d\phi = nh$$

If L is constant we have

$$L \cdot 2\pi = nh$$

$$L = \frac{nh}{2\pi} = n\hbar \text{ where } n = 0, 1, 2, \dots$$

Allowed energy values are therefore

$$E_n = \frac{L^2}{2I} = \frac{n^2 \hbar^2}{2I}$$

where E_n is the kinetic energy. This picture is due to old quantum theory. But this theory has been superseded by the new quantum theory or quantum mechanics.

To get the allowed energy values in the realm of quantum mechanics we have to solve the schrodinger for the rigid rotator. This gives

$$E_l = \frac{\hbar^2}{2I} l(l+1), \quad l = 0, 1, 2, 3, \dots$$

where l is the orbital quantum number.

Evaluation of I of a rigid rotator

The moment of inertia of the rigid rotator about an axis passing through its centre of mass and perpendicular to the molecular axis

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots (1)$$

From the concept of centre of mass of two particle system, we have

$$m_1 r_1 = m_2 r_2$$

Using $r_1 + r_2 = r$ (see figure)

$$r_2 = r - r_1$$

$$\therefore m_1 r_1 = m_2 (r - r_1)$$

or $r_1(m_1 + m_2) = m_2 r$

$$r_1 = \frac{m_2 r}{m_1 + m_2}$$

Similarly $r_2 = \frac{m_1 r}{m_1 + m_2}$

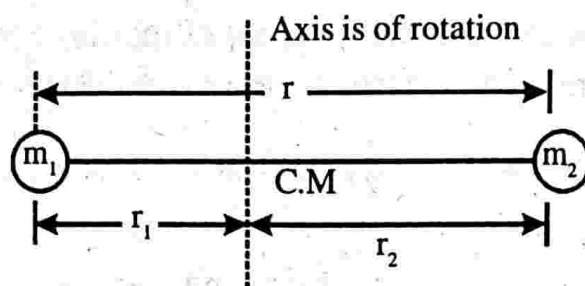


Figure 4.5

Putting the values of r_1 and r_2 in equn. (1) we get

$$I = m_1 \left(\frac{m_2 r}{m_1 + m_2} \right)^2 + m_2 \left(\frac{m_1 r}{m_1 + m_2} \right)^2$$

$$I = \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r^2}{(m_1 + m_2)^2} = \frac{m_1 m_2 r^2 (m_1 + m_2)}{(m_1 + m_2)^2}$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

Rotational spectrum of rigid diatomic molecule

We could see that a molecule can be considered as a rigid rotator. The energy eigen value is given by

$$E_J = \frac{\hbar^2}{2I} J(J+1), \quad J = 0, 1, 2, \dots$$

where J is the rotational quantum number (the angular momentum quantum number l is redesignated as J just to follow the standard symbols used in standard spectroscopy text books). To analyse the rotational spectrum energy is expressed in wave number (ϵ_j) units for convenience.

$$\epsilon_j = \frac{1}{\lambda} = \frac{v}{c} = \frac{h\nu}{hc} = \frac{E_j}{hc}$$

or
$$\epsilon_j = \frac{\hbar^2 J(J+1)}{2I hc} = \frac{\hbar}{4\pi Ic} J(J+1) = \frac{h}{8\pi^2 Ic} J(J+1)$$

$$\epsilon_J = BJ(J+1) \quad \dots (1)$$

where B is the rotational constant and is given by

$$B = \frac{h}{8\pi^2 I c} \quad \dots (2)$$

If h , I and c are expressed in cgs, B has the unit cm^{-1} .

From eqn. (1), we can draw the energy level diagram. See figure below.

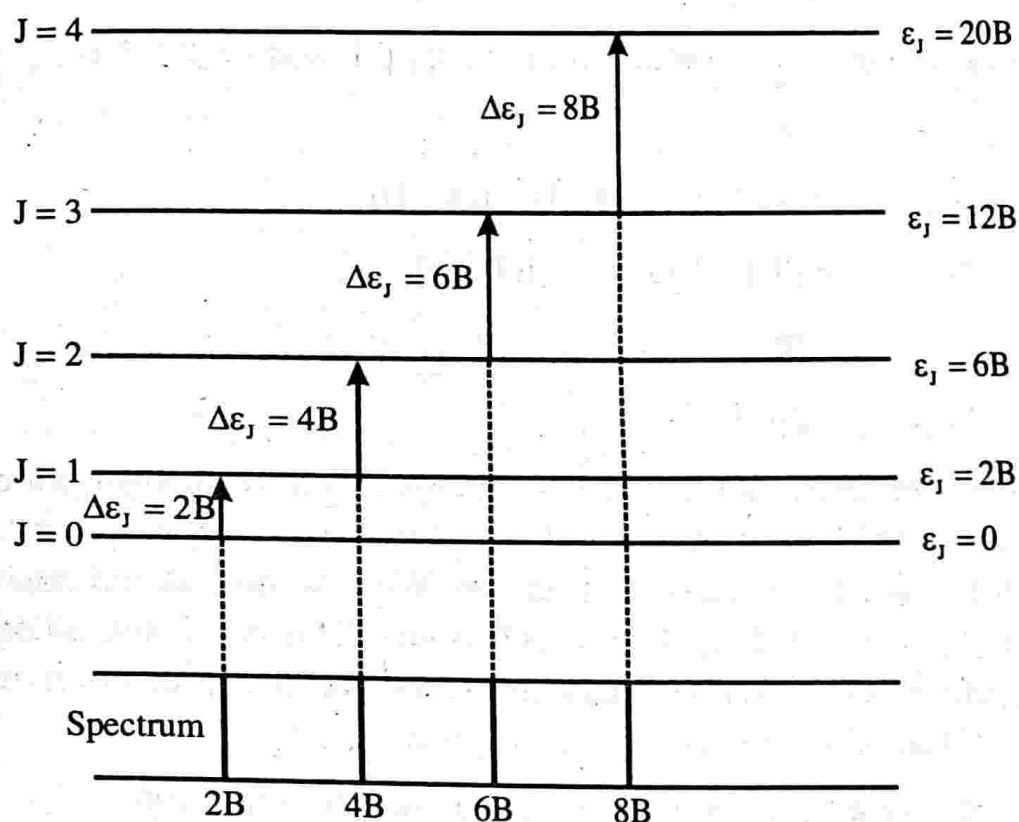


Figure 4.6 : Rotational energy levels and transitions for a rigid diatomic molecule

Denoting the lower state by J'' and upper state by J' , From eqn (1) we get

$$\epsilon_{J'} = B = J'(J' + 1) \quad \dots (3)$$

$$\epsilon_{J''} = B = J''(J'' + 1) \quad \dots (4)$$

Eqn (3)-Eq (4) gives

$$\epsilon_{J'} - \epsilon_{J''} = B [J'(J' + 1) - J''(J'' + 1)]$$

$$\Delta\epsilon_J = B[J'(J' + 1) - J''(J'' + 1)] \quad \dots (5)$$

If we imagine the molecule to be in the ground rotational state ($J'' = 0$) and let the incident radiation be absorbed to raise it to the next higher state ($J' = 1$). Then

$$\Delta\epsilon_{J=0 \rightarrow 1} = 2B$$

If the molecule is raised from $J = 1$ to $J = 2$ (i.e., $J'' = 1$ and $J' = 2$)

$$\Delta\epsilon_{J=1 \rightarrow 2} = B = [2(2+1) - 1(1+1)]$$

$$\Delta\epsilon_{J=1 \rightarrow 2} = 4B$$

If the molecule is raised from $J = 2$ to $J = 3$ (i.e., $J'' = 2$ and $J' = 3$)

$$\Delta\epsilon_{J=2 \rightarrow 3} = 6B$$

In general, to raise the molecule from the state J to state $J + 1$ (i.e., $J'' = J$ and $J' = J + 1$)

$$\therefore \Delta\epsilon_{J \rightarrow J+1} = B[(J+1)(J+1+1) - J(J+1)]$$

$$\Delta\epsilon_{J \rightarrow J+1} = B[(J+1)(J+2) - J(J+1)]$$

$$= B[J^2 + 3J + 2 - J^2 - J]$$

$$\Delta\epsilon_{J \rightarrow J+1} = 2B(J+1) \quad \dots (6)$$

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of spectral lines at $2B, 4B, 6B, \dots$. Similarly a stepwise lowering of the rotational energy results in emission spectrum. We have considered raising or lowering to the immediate level i.e., J changes by unity. This is because all other transitions are spectroscopically forbidden. Such a result is called a selection rule. For the rigid rotator (Diatomic) the selection rule is given by

$$\Delta J = \pm 1, \text{ plus sign for absorption and minus sign for emission.}$$

From the spectral lines obtained, the value of B can be deduced from the spacing between the lines. Knowing B , I can be evaluated using equation 2. From the value of $I(\mu r^2)$, the internuclear distance (r) of the diatomic molecule can be calculated.

Bond length of CO and the valid of the theory

Gilliam, Johnson and Gordy have measured the first line ($J = 0$) in the rotation spectrum of carbon monoxide as 3.84235 cm^{-1} . From eqn (6), we have

$$\Delta E_{J=0 \rightarrow 1} = 3.84235 = 2B$$

$$\therefore B = 1.92118 \text{ cm}^{-1}$$

$$\therefore I = \frac{h}{8\pi^2 c B} \quad \left(\because B = \frac{h}{8\pi^2 I c} \right)$$

$$I = \frac{6.626 \times 10^{-34} \text{ kgm}^2}{8 \times 3.14^2 \times 2.99793 \times 10^{10} \times 1.92118}, \text{ here } B \text{ is in cm}^{-1} \text{ and } c \text{ is in cm s}^{-1}$$

$$I = 14.5695 \times 10^{-47} \text{ kgm}^2$$

Using $I = \mu r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2 = \frac{m_c m_o}{m_c + m_o} r^2$

$$\frac{m_c m_o}{m_c + m_o} = \frac{19.92178 \times 10^{-27} \times 26.5613 \times 10^{-27}}{(19.92178 + 26.5613) \times 10^{-27}}$$

$$= 11.38365 \times 10^{-27} \text{ kg}$$

$$r^2 = \frac{I}{\mu} = \frac{14.5695 \times 10^{-47}}{11.38365 \times 10^{-27}} = 1.2799 \times 10^{-20} \text{ m}^2$$

$$r_{co} = 0.1131 \text{ nm} = 1.131 \text{ \AA}$$

This is in well agreement with the experimental results.

Note :- Knowing the relative atomic weights to be C = 12 and O = 15.9994 if H = 1.0080.

Absolute mass of hydrogen atom = $1.67343 \times 10^{-27} \text{ kg}$

$$m_c = \frac{12 \times 1.67343 \times 10^{-27}}{1.008} = 19.92178 \times 10^{-27} \text{ kg}$$

and $m_o = \frac{15.9994 \times 1.67343 \times 10^{-27}}{1.008} = 26.5613 \times 10^{-27} \text{ kg}.$

Intensities of spectral lines

The pure rotational spectrum of a diatomic molecule is due to the change in rotational energy levels. These energy levels are quantised. When a molecule rotates from its allowed rotational energy level to the nearest allowed energy level, a spectrum (equally spaced spectral lines) is obtained. The allowed transitions are governed by the selection rule $\Delta J = \pm 1$. Here our aim is to estimate the relative intensities of spectral lines. The intensity of a spectral lines depends upon the number of molecules present in each level. This is given by Boltzmann's distribution function. Moreover each level is $(2J + 1)$ fold degenerate. (see foot note)

If N_J is the number of molecules in the J^{th} state we have

$$N_J \propto (2J+1)e^{-\frac{E_J}{kT}}$$

or
$$N_J \propto (2J+1)e^{-\frac{Bhc J(J+1)}{kT}}$$

where
$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ with } B = \frac{h}{8\pi^2 Ic}$$

when N_J is plotted against J , we get a graph as shown below. The curve shows that the population rises to a maximum then diminishes. Maximum population means maximum intensity. In other words intensity will be maximum corresponding to nearest integral J value.

To get to the J value corresponding to maximum N_J , differentiate N_J with respect to J and put equal to zero.

We have

$$N_J = A(2J+1)e^{-DJ(J+1)}$$

where
$$D = \frac{Bhc}{kT}$$

$$\therefore \frac{dN_J}{dJ} = A(2J+1)e^{-DJ(J+1)} \times -D(2J+1) + 2Ae^{-DJ(J+1)}$$

$$0 = -AD(2J+1)^2 e^{-DJ(J+1)} + 2Ae^{-DJ(J+1)}$$

or
$$AD(2J+1)^2 e^{-DJ(J+1)} = 2Ae^{-DJ(J+1)}$$

or
$$D(2J+1)^2 = 2$$

$$(2J+1)^2 = \frac{2}{D}$$

$$(2J+1) = \sqrt{\frac{2}{D}}$$

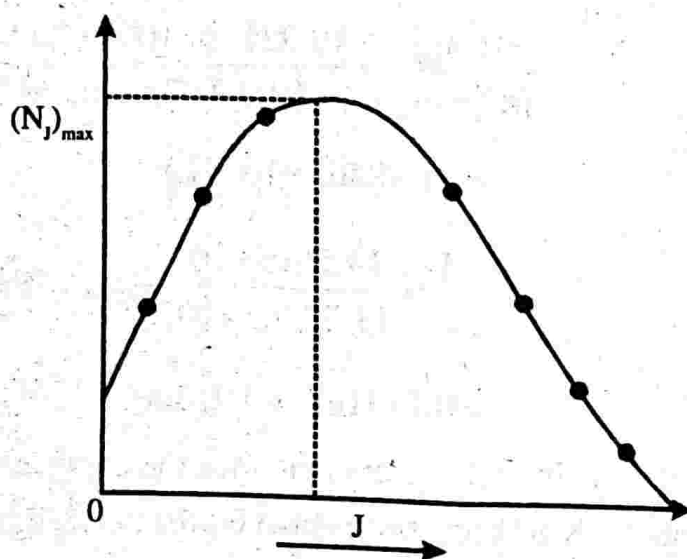


Figure 4.7

$$2J = \sqrt{\frac{2}{D}} - 1$$

$$\therefore J = \sqrt{\frac{1}{2D}} - \frac{1}{2}$$

Putting the value of D

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

The transition from this level will have maximum intensity.

Degeneracy of energy level

An energy level is said to be degenerate if there exists two or more levels corresponding to same energy. The number of energy levels possible with same energy is called degeneracy. Here we shall estimate the degeneracy of a rigid rotator for a given J value. The energy and angular momentum of a rigid rotator are given by

$$E = \frac{1}{2} I \omega^2 \text{ and } L = I \omega$$

or
$$E = \frac{1}{2} \frac{I^2 \omega^2}{I} = \frac{L^2}{2I}$$

or
$$\bar{L} = \sqrt{2EI} \quad \dots (1)$$

Putting the expression for E

$$\bar{L} = \sqrt{2 \times \frac{\hbar^2}{2I} J(J+1)} = \hbar \sqrt{J(J+1)}$$

$$\bar{L} = \sqrt{J(J+1)} \quad \dots (2)$$

\hbar is taken as the unit of angular momentum.

Equation (1) shows that same energy level means same angular momentum vector. For a given J, \bar{L} has a constant value according to equation 2. Since \bar{L} being a vector this constant vector length will have different orientations with respect to a given reference direction.

when $J=1$ $\bar{L} = \sqrt{2}$

A vector length $\sqrt{2}$ can have three orientations with respect to reference direction. (see figure below). i.e., $J=1$ is three fold degenerate.

Similarly for $J=2$, $\bar{L} = \sqrt{6}$, we get 5 different orientations and for $J=3$, $\bar{L} = \sqrt{12}$ we get 7 different orientations. In general we can say for a given J , there are $2J+1$ orientations. see figure below.

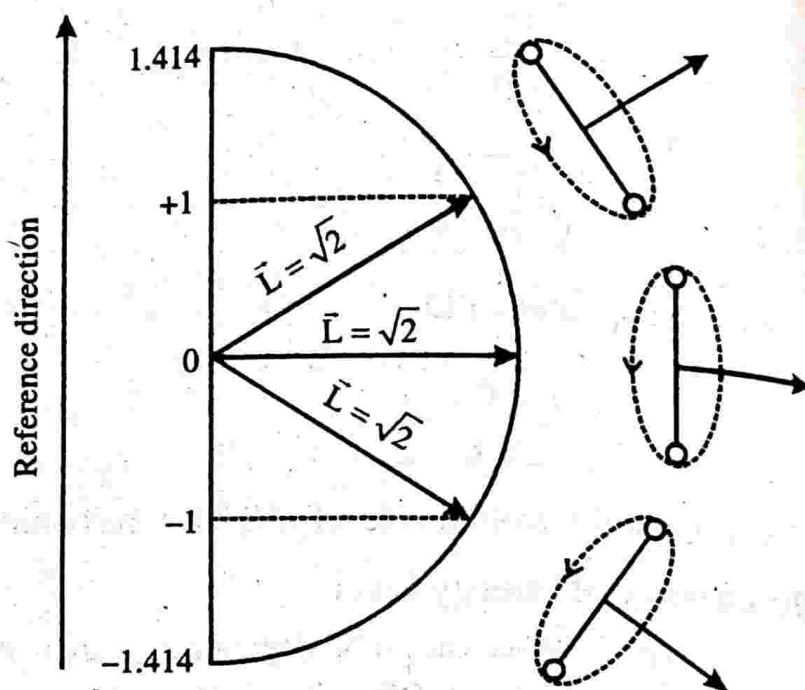


Figure 4.8

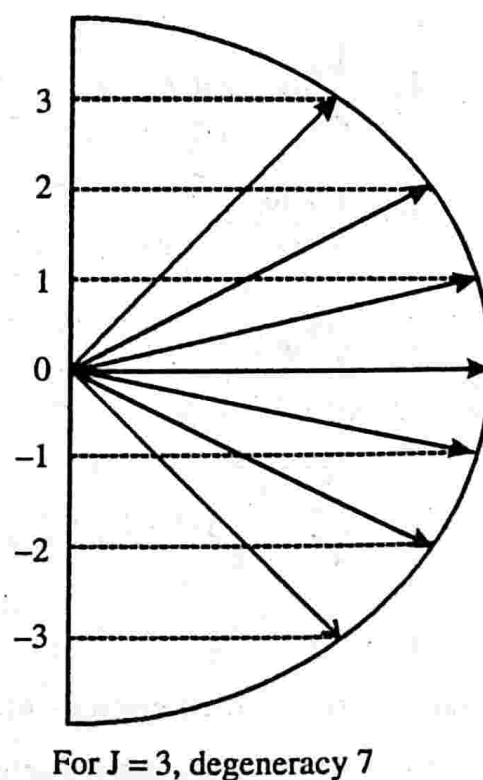
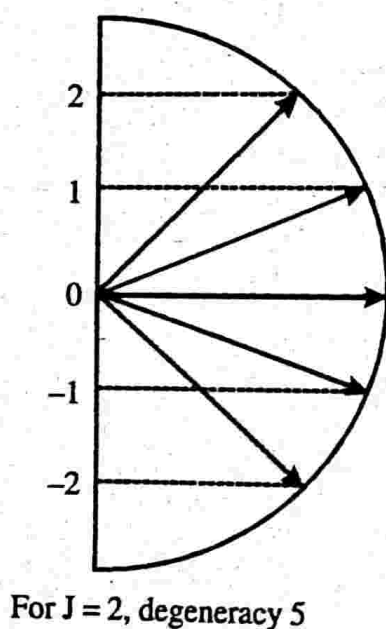


Figure 4.9

Example 1

What is the change in rotational constant B when hydrogen is replaced by deuterium in hydrogen molecule.

Solution

We have $B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 \mu r^2 c}$

or $B \propto \frac{1}{\mu}$

For hydrogen molecule $\mu = \frac{m_H m_H}{m_H + m_H} = \frac{m_H}{2}$

$\therefore B \propto \frac{2}{m_H}$ (1)

When one hydrogen is replaced by deuterium

$B' \propto \frac{1}{\mu'}$

For deuterium $\mu' = \frac{m_D m_D}{m_D + m_D} = \frac{m_D}{2} = \frac{2m_H}{2} = m_H$

$\therefore B' \propto \frac{1}{m_H}$ (2)

$\frac{\text{Eq(2)}}{\text{Eq(1)}} \rightarrow \frac{B'}{B} = \frac{1}{2}$

or $B' = \frac{B}{2}$

\therefore Change in rotational constant

$B - B' = B - \frac{B}{2} = \frac{B}{2}$

Example 2

The rotational constant for H^{35}Cl is found to be 10.5909 cm^{-1} . What is the value of B for H^{37}Cl .

Solution

$$B = 10.5909 \text{ cm}^{-1} \text{ for } \text{H}^{35}\text{Cl}.$$

If B' is the rotational constant for H^{37}Cl .

Then we have

$$\frac{B'}{B} = \frac{\mu}{\mu'} \quad \left(\because B \propto \frac{1}{\mu} \right)$$

$$\mu = \frac{m_{\text{H}} \times {}^{35}\text{m}_{\text{Cl}}}{m_{\text{H}} + {}^{35}\text{m}_{\text{Cl}}} = \frac{m_{\text{H}} \times 35m_{\text{H}}}{m_{\text{H}} + 35m_{\text{H}}} = \frac{35}{36} m_{\text{H}}$$

$$\mu' = \frac{m_{\text{H}} \times {}^{37}\text{m}_{\text{Cl}}}{m_{\text{H}} + {}^{37}\text{m}_{\text{Cl}}} = \frac{37}{38} m_{\text{H}}$$

$$\therefore \frac{B'}{B} = \frac{35}{36} \times \frac{38}{37} = 0.9985$$

$$\text{or } B' = 0.9985 \times B = 9985 \times 10.5909 \\ = 10.5750 \text{ cm}^{-1}$$

Example 3

The microwave spectrum of CN radical shows a series of lines spaced by a nearly constant amount of 3.798 cm^{-1} . What is the bond length of CN?

Solution

$$2B = 3.798 \text{ cm}^{-1} \text{ (given)}$$

$$B = 1.899 \text{ cm}^{-1}$$

$$\text{Using } B = \frac{h}{8\pi^2 Ic}$$

$$I = \frac{h}{8\pi^2 Bc}$$

$$I = \frac{6.626 \times 10^{-34}}{8 \times \pi^2 \times 1.899 \times 3 \times 10^{10}} \text{ kgm}^2$$

$$I = 14.7304 \times 10^{-47} \text{ kgm}^2$$

We have

$$I = \mu r^2$$

$$\mu = \frac{m_C \times m_N}{m_C + m_N} = \frac{12m_H \times 14.003m_H}{12m_H + 14.003m_H} = 6.4622m_H$$

$$\mu = \frac{6.4622}{1.008} \times 1.67343 \times 10^{-27} \text{ kg}$$

$$= 10.7282 \times 10^{-27} \text{ kg}$$

$$r = \sqrt{\frac{14.7304 \times 10^{-47}}{10.7282 \times 10^{-27}}} = 1.1718 \times 10^{-10} \text{ m}$$

$$r = 1.1718 \text{ \AA}$$

Example 4

How many revolutions per second does a CO molecule make when $J = 3$. The CO bond length is 0.1131 nm. Avagadro number 6.022×10^{23} .

Solution

$$r = 0.1131 \times 10^{-9} \text{ m}$$

Reduced mass of CO molecule

$$\mu = \frac{m_C \times m_O}{m_C + m_O} = \frac{12 \times 15.9949}{(12 + 15.9949) \times 6.022 \times 10^{23}} \text{ g}$$

$$\mu = 1.1385 \times 10^{-26} \text{ kg}$$

$$I = \mu r^2 = 1.1385 \times 10^{-26} \times (0.1131 \times 10^{-9})^2$$

$$= 0.1456 \times 10^{-45} \text{ kgm}^2$$

We have rotational energy

$$\frac{1}{2} I \omega^2 = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$\omega = \frac{h \sqrt{J(J+1)}}{2\pi I}$$

$$\nu = \frac{h\sqrt{J(J+1)}}{4\pi^2 I}$$

$$\nu = \frac{6.626 \times 10^{-34} \sqrt{3(3+1)}}{4 \times \pi^2 \times 0.1456 \times 10^{-45}}$$

$$\nu = 39.93 \times 10^{10} \text{ Hz}.$$

Example 5

The first rotational line of $^{12}\text{C}^{16}\text{O}$ is observed at 3.84235cm^{-1} and that of $^{13}\text{C}^{16}\text{O}$ at 3.67337cm^{-1} . Calculate the atomic weight of ^{13}C , assuming the mass of ^{16}O to be 15.9949.

Solution

$$B = 3.84235 \quad \text{— for } ^{12}\text{C}^{16}\text{O}$$

$$B' = 3.67337 \quad \text{— for } ^{13}\text{C}^{16}\text{O}$$

$$\frac{B}{B'} = \frac{\mu'}{\mu}$$

$$\text{But } \mu = \frac{{}^{12}m_{\text{C}} \times m_{\text{O}}}{{}^{12}m_{\text{C}} + m_{\text{O}}} = \frac{12 \times 15.9949}{(12 + 15.9949)(6.02 \times 10^{23})}$$

$$\mu' = \frac{{}^{13}m_{\text{C}} \times m_{\text{O}}}{{}^{13}m_{\text{C}} + m_{\text{O}}} = \frac{m \times 15.9949}{(m + 15.9949)(6.02 \times 10^{23})}$$

$$\frac{\mu'}{\mu} = \frac{m \times 15.9949}{m + 15.9949} \times \frac{27.9949}{12 \times 15.9949}$$

Substituting B, B', μ and μ' in eqn (1), we get

$$\frac{3.84235}{3.67337} = \frac{m \times 15.9949}{m + 15.9949} \times \frac{27.9949}{12 \times 15.9949}$$

$$1.046 = \frac{m \times 15.9949}{m + 15.9949} \times 0.14585$$

$$\frac{1.046}{0.14585} = \frac{15.9949m}{m + 15.9949}$$

$$7.1715m + 7.17175 \times 15.9949m$$

$$7.1715 \times 15.9949 = 15.9949m - 7.17175m$$

$$114.71142 = 8.82315m$$

$$m = \frac{114.71142}{8.82315} = 13.001$$

Atomic weight of ^{13}C is 13.001

Example 6

The average spacing between successive rotational line of carbon monoxide is 3.8626 cm^{-1} . Determine the transition which gives the most intense spectral line at 300K.

Solution

$$2B = 3.8626\text{ cm}^{-1} \text{ (given)}$$

$$B = 1.9313\text{ cm}^{-1}$$

$$T = 300\text{ K}$$

For the most intense spectral line

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

$$J = \sqrt{\frac{1.381 \times 10^{-23} \times 300}{2 \times 6.626 \times 10^{-34} \times 3 \times 10^{10} \times 1.9313}} - \frac{1}{2}$$

$$J = 7.3456 - 0.5$$

$$J = 6.8456$$

Therefore most intense line is obtained for $J = 7$.

Example 7

The $J = 0 \rightarrow 1$ transition in HCl occurs at 20.68 cm^{-1} . Regarding the molecule to be a rigid rotator, calculate the wavelength of the transition $J = 14 \rightarrow 15$.

Solution

$$2B = 20.68 \text{ cm}^{-1}$$

$$B = 10.34 \text{ cm}^{-1}$$

We have

$$\epsilon_j = 2B(J+1)$$

$$\epsilon_j = 2 \times 10.34(14+1) = 310.2 \text{ cm}^{-1}$$

$$\therefore \text{Wavelength } \lambda = \frac{1}{\epsilon_j} = \frac{1}{310.2} = 32 \times 10^{-4} \text{ cm}$$

$$\lambda = 32 \times 10^{-6} \text{ m}$$

Example 8

The OH radical has a moment of inertia of $1.48 \times 10^{-47} \text{ kgm}^2$. Calculate its inter-nuclear distance. Also calculate for $J = 5$, its angular momentum and angular velocity.

Solution

$$I = 1.48 \times 10^{-47} \text{ kgm}^2$$

$$\mu = \frac{m_H \times m_O}{m_H + m_O} = \frac{1 \times 16}{(1+16) 6.023 \times 10^{26}}$$

$$\mu = 1.563 \times 10^{-27} \text{ kg}$$

Using $I = \mu r^2$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.48 \times 10^{-47}}{1.563 \times 10^{-27}}} = 9.731 \times 10^{-11} \text{ m}$$

Angular momentum is given by

$$L = \frac{h}{2\pi} \sqrt{J(J+1)}$$

$$L = \frac{6.62 \times 10^{-34} \sqrt{J(J+1)}}{2 \times 3.14} = 5.77 \times 10^{-34} \text{ Js}$$

$$\omega = \frac{L}{I} = \frac{5.77 \times 10^{-34}}{1.48 \times 10^{-47}} = 3.9 \times 10^{13} \text{ rads}^{-1}$$

IMPORTANT FORMULAE

1. The allowed rotational energy levels of a rigid diatomic molecule.

$$E_J = \frac{\hbar^2}{2I} J(J+1), J = 0, 1, 2, \dots$$

where

$$I = \mu r^2 \text{ with } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

In terms of wave number

$$\epsilon_J = BJ(J+1), \epsilon_J = \frac{1}{\lambda}$$

where

$$B = \frac{h}{8\pi^2 Ic}$$

2. The value of rotational quantum number (J) corresponding to maximum intensity.

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

3. The angular momentum of a rigid diatomic molecule.

$$\bar{L} = J(J+1)\hbar$$

4. The frequency of diatomic molecule

$$\nu = \frac{h\sqrt{J(J+1)}}{4\pi^2 I}$$

5. Selection rule for rotational spectrum.

$$\mu_{ij} \neq 0, \Delta J = \pm 1$$

6. The number of molecules in the J^{th} state

$$N_J \propto (2J+1)e^{-\frac{E_J}{kT}}$$

where $E_J = BhcJ(J+1)$ with $B = \frac{h}{8\pi^2 Ic}$.

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in two or three sentences)

Short answer type questions

1. Classify molecules according to their rotational inertia.
2. What is a linear molecule? Give two examples.
3. What is a symmetric top molecule? Give two examples.
4. What is a spherical top molecule? Give two examples.
5. What are asymmetric tops? Give two examples.
6. Spherical top molecules do not show rotational spectrum. Explain why?
7. Distinguish between prolate and oblate symmetric top molecules.
8. What is a rigid rotator?
9. Comment on rotational quantum number.
10. Write down the expression for energy eigen value of a rigid rotator and explain the symbols.
11. What is rotational constant? How does it influence a spectrum?
12. Draw the rotational energy levels and transitions for a rigid diatomic molecule.
13. What is a selection rule? What is it for a rigid rotator?
14. What are the factors on which the intensity of rotational spectra depend.
15. What is meant by degeneracy of eigen value?
16. How does the elasticity of bond length influence the rotational constant?
17. Give two informations derived from rotational spectra.
18. How will you evaluate the bond length of a molecule from rotational constant?
19. Write down the selection rule for the molecular spectrum of rigid symmetric top molecule.
20. Depict a schematic representation of energy levels and transitions for the rigid prolate and the rigid oblate symmetric top molecules.
21. Write down the equation for the energy levels of rigid prolate symmetric top molecule.

Section B

(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type questions

1. Briefly explain how does electromagnetic radiation interact with rotating molecule.
2. Molecules having permanent dipole moment exhibit rotational spectrum. Explain why.
3. Evaluate the moment of inertia of a diatomic molecule.
4. Derive an expression for the rotational constant B.

5. How will you establish the validity of the theory of rotation spectra of rigid diatomic molecule?
6. Derive an expression for the rotational quantum number corresponding to maximum intensity rotational spectra.
7. What is the change in rotational constant B when ^{12}C of carbon monoxide ($^{12}\text{C } ^{16}\text{O}$) is replaced by ^{13}C . B of $^{12}\text{C } ^{16}\text{O}$ is 1.92118cm^{-1} . [0.08449]
8. The rotational constant of H^{35}Cl is found to be 10.5009cm^{-1} . What is the value of $^2\text{D } ^{35}\text{Cl}$? [5.446 cm^{-1}]
9. How many revolutions per second does CO molecule make when $J = 4$? The rotational constant of CO molecule is 1.9313cm^{-1} . [$51.822 \times 10^{10}\text{ Hz}$]
10. The separation between lines in the rotational spectrum of HCl molecule was found to be 20.92cm^{-1} . Calculate the bond length. [1.282Å]
11. The rotational spectrum of $^{79}\text{Br } ^{19}\text{F}$ shows a series of equidistant lines 0.71433cm^{-1} apart. Calculate the rotational constant B, and hence moment of inertia and bond length of the molecule. $^{79}\text{Br} = 131.03 \times 10^{-27}\text{ kg}$, $^{19}\text{F} = 31.55 \times 10^{-27}\text{ kg}$.
[$B = 0.35717\text{cm}^{-1}$, $I = 7.837 \times 10^{-46}\text{ kgm}^2$, $r = 1.756 \times 10^{-10}\text{ m}$]
12. In the above problem find which transition gives rise to the most intense spectral line at temperature 300K. [$J = 17$]
13. Evaluate the moment of inertia of a rigid rotator
$$\left[I = \frac{m_1 m_2}{m_1 + m_2} r^2 \right]$$
14. Find the expression for the J value for which intensity of spectral line is maximum.
15. Calculate the rotational energy levels of HCl molecule in eV. Given bond length $r = 0.13\text{nm}$ [$1.26 \times 10^{-3}\text{ J}(J+1)\text{eV}$]
16. The moment of inertia of the CO molecule is $1.46 \times 10^{-46}\text{ kgm}^2$. Calculate the energy in eV, and the angular velocity in the lowest rotational energy level of the CO molecule. [$4.74 \times 10^{-4}\text{ eV}$, $1.0193 \times 10^{12}\text{ rad/s}$]

Section C

(Answer questions in about two pages)

Long answer type questions (Essays)

1. Obtain an expression for the rotational energy levels of a diatomic molecule taking it as a rigid rotator.

Hints to problems

1 to 6 See book work

$$7. \quad \frac{B}{B'} = \frac{\mu'}{\mu}, \quad \mu = \frac{{}^{12}m_C \times m_O}{{}^{12}m_C + m_O}, \quad {}^{12}m_C = 12, \quad m_O = 15.9994$$

$$\mu' = \frac{{}^{13}m_C \times m_O}{{}^{13}m_C + m_O}, \quad {}^{13}m_C = 13.001$$

$$\frac{\mu'}{\mu} = 1.046$$

$$\text{i.e., } \frac{B}{B'} = 1.046$$

$$B' = \frac{B}{1.046}, \quad B = 1.92118$$

\therefore Change in $B = B - B'$

8. See example 2

$$9. \quad \frac{1}{2}I\omega^2 = \frac{h^2}{8\pi^2I}J(J+1)$$

$$\omega^2 = \frac{h^2}{4\pi^2I^2}J(J+1) \quad \text{use } B = \frac{h^2}{8\pi^2Ic} \quad B^2 = \frac{h^2}{64\pi^4I^2c^2}$$

$$\omega^2 = 16\pi^2c^2B^2J(J+1)$$

$$\omega = 4\pi cB\sqrt{J(J+1)}$$

$$2\pi\nu = 4\pi cB\sqrt{J(J+1)}$$

$$\nu = 2cB\sqrt{J(J+1)}$$

$$\nu = 2 \times 3 \times 10^{10} \times 1.9313cB\sqrt{4 \times (4+1)}$$

$$\nu = 51.822 \times 10^{10} \text{ Hz (see also example 4)}$$

10. $2B = 20.92 \text{ cm}^{-1}$ given

$$\text{Using } B = \frac{h}{8\pi^2Ic}$$

$$I = \frac{h}{8\pi^2Bc} = \frac{6.626 \times 10^{-34}}{8 \times \pi^2 \times 10.46 \times 3 \times 10^{10}}$$

$$I = 2.6743 \times 10^{-47} \text{ kgm}^2$$

$$I = \mu r^2$$

$$\therefore r = \sqrt{\frac{I}{\mu}}$$

$$\mu = \frac{m_H \times m_{Cl}}{m_H + m_{Cl}} = \frac{1.673 \times 10^{-27} \times 58.06 \times 10^{-27}}{(1.673 + 58.06) \times 10^{-27}}$$

$$\mu = 1.6261 \times 10^{-27} \text{ kg}$$

11. See example 3

12. See example 6

13. See book work

14. See book work

$$15. \mu = \frac{1.008 \times 35.46}{1.008 + 35.46 \times 6.023 \times 10^{26}} 1.627 \times 10^{-27} \text{ kg}$$

$$I = \mu r^2 = 1.627 \times 10^{-27} \times (0.13 \times 10^{-9})^2 = 2.75 \times 10^{-47} \text{ kgm}^2$$

$$E_j = \frac{h^2}{8\pi^2 I} J(J+1) = \frac{(6.616 \times 10^{-34})^2 J(J+1)}{8\pi^2 \times 2.75 \times 10^{-47} \times 1.6 \times 10^{-19}}$$

$$16. E_j = \frac{h^2}{8\pi^2 I} J(J+1), J=1 \text{ given}$$

Find E_j and convert into eV.

$$E_j = \frac{1}{2} I \omega^2$$

or

$$\omega = \sqrt{\frac{2E_j}{I}}$$
